Velocity Fluctuations of a Hard-Core Brownian Particle*

Allan Widom
Northeastern University, Physics Department, Boston, Massachusetts 02115
(Received 30 October 1970)

The velocity autocorrelation function $\langle v(t)\,v(0)\rangle$ of a hard-sphere Brownian particle moving in an incompressible viscous fluid is calculated on the basis of hydrodynamics. The usually assumed exponential decay at long times is shown to be inconsistent with fluid mechanics. A slower decay $\propto t^{-3/2}$ as $t\to\infty$ is derived. This decay has been observed in molecular dynamic computations carried out by Alder and Wainwright.

I. INTRODUCTION

The Brownian motion of a large massive impurity in a classical liquid is well known as direct evidence of thermal molecular motion. In Einstein's classic investigations,[1] it was pointed out that the diffusion coefficient

$$D=\lim_{t\to\infty}\left(\frac{\langle\Delta x(t)^2\rangle}{2t}\right)=\int_0^\infty \langle v(t)v(0)\rangle\, dt \qquad (1)$$

is simply related to the mobility μ:

$$\mu=D/kT\ . \qquad (2)$$

Einstein considered a hard sphere of mass M and radius R moving through an incompressible fluid of mass density ρ and viscosity η as a model Brownian particle. The mobility is then given by Stokes's law:

$$\mu^{-1}=6\pi\eta R\ . \qquad (3)$$

The experimental validity of the relation $D=kT/6\pi\eta R$ strongly supports the physical reality of this model.

It is interesting to note that Einstein made no hypothesis about the behavior of the velocity autocorrelation function

$$\phi(t-s)=\langle v(t)v(s)\rangle\ . \qquad (4)$$

Assuming the stochastic random variable $v(t)$ is Gaussian and Markovian, it follows[2] that $\phi(t)$ is exponentially decaying. Although this leads to an important mathematical theory,[3] the basic assumptions are physically unproven both theoretically (from microscopic dynamics) and experimentally. The detailed time dependence of $\phi(t)$ has not yet been observed in the laboratory.

The purpose of this paper is to point out the following: (i) Fluid mechanics makes a definite prediction about the behavior of the velocity autocorrelation function $\phi(t)$; (ii) the prediction is valid in the limit $t\to\infty$; and (iii) the usually assumed exponential decay is too fast; the actual decay is $\phi(t)\sim t^{-3/2}$ as $t\to\infty$.

II. EQUATION OF MOTION

The drag force on a hard sphere moving with velocity $u(t)$ in an incompressible fluid is given by[4]

$$F(t)=-6\pi\eta Ru(t)-\tfrac{2}{3}\pi\rho R^3\,\dot{u}(t)-6R^2(\pi\eta\rho)^{1/2}\int_{-\infty}^t (t-s)^{-1/2}\dot{u}(s)\,ds\ . \qquad (5)$$

When $\dot{u}(t)=0$, Eq. (5) yields the Stokes mobility given in Eq. (3). When $\dot{u}(t)\neq 0$, the last two terms on the right-hand side of Eq. (5) become important.

Suppose that an external force $f_{ext}(t)$ acts on the Brownian impurity. The total force equals the external force plus the drag force:

$$M\dot{u}(t)=f_{ext}(t)+F(t)\ . \qquad (6)$$

On the other hand, linear-response theory[5] predicts that

$$u(t)=(kT)^{-1}\int_{-\infty}^t \phi(t-s)f_{ext}(s)\,ds\ . \qquad (7)$$

The equation of motion for $\phi(t)$ follows from Eqs. (5)–(7) and the initial condition

$$\phi(0)=\langle v^2\rangle=kT/M\ . \qquad (8)$$

It is

$$M^*\dot{\phi}(t)=-6\pi\eta R\phi(t)-6R^2kT(\pi\eta\rho/tM^2)^{1/2}-(6R^2kT/M)(\pi\eta\rho)^{1/2}\int_0^t (t-s)^{1/2}\dot{\phi}(s)\,ds\ , \qquad (9)$$

where the effective mass of the impurity is given by

$$M^*=M+\tfrac{2}{3}\pi\rho R^3\ . \qquad (10)$$

Trying a solution of the form

$$\phi(t)=(kT/M)\left[1-\int_0^{\gamma t}\psi(x)\,dx\right]\ , \qquad (11)$$

where

$$\gamma=6\pi\eta R/M^*\ , \qquad (12)$$

yields the integral equation

$$\psi(x)+\int_0^x g(x-y)\psi(y)\,dy=g(x)\ . \qquad (13)$$

In Eq. (13)

$$g(x)=1+\alpha(\pi x)^{-1/2}\ , \qquad (14)$$

$$\alpha^2 = 6\pi\rho R^3/M^* \ . \tag{15}$$

From Eqs. (10) and (15) it follows that the physical values of the dimensionless parameter α are in the range

$$0 < \alpha < 3 \ . \tag{16}$$

Equation (13) is a Volterra integral equation of the second kind and of the Faltung type.[6] It is solved by transform techniques.

III. SOLUTION OF INTEGRAL EQUATION

Let

$$f(\zeta) = \int_0^\infty e^{-\zeta^2 x}\psi(x)\,dx \ , \quad \zeta > 0 \ . \tag{17}$$

From (i) the obvious indentity [see Eq. (14)]

$$\int_0^\infty e^{-\zeta^2 x} g(x)\,dx = (1/\zeta^2) + \alpha(1/\zeta) \ , \tag{18}$$

(ii) the convolution theorem for Laplace transforms, and (iii) Eq. (13), it follows that

$$f(\zeta) = \frac{1+\alpha\zeta}{1+\alpha\zeta+\zeta^2} \ . \tag{19}$$

Furthermore, let

$$\chi(\sigma) = \int_0^\infty 2\zeta f(\zeta) e^{-\zeta^2\sigma}\,d\zeta \ , \quad \sigma > 0 \ . \tag{20}$$

Equations (17) and (20) imply

$$\chi(\sigma) = \int_0^\infty \frac{\psi(x)\,dx}{x+\sigma} \ . \tag{21}$$

Considered as a function of a complex variable, $\chi(\sigma)$ is analytic in the σ plane with a cut on the negative axis. The discontinuity across this cut is determined by $\psi(x)$. Since $\psi(x)$ is real, a dispersion relation follows:

$$\psi(x) = -(1/\pi)\lim_{\epsilon\to 0^+} \operatorname{Im}\chi(\sigma = -\chi + i\epsilon) \ . \tag{22}$$

The solution of Eq. (13) can now be found in the following manner: (i) Evaluate Eq. (20) for real positive values of σ in a form that can be analytically continued into the complex σ plane. (ii) The solution of the integral equation is found from the dispersion relation in Eq. (22).

From Eqs. (19) and (20) it follows that

$$\chi(\sigma) = \int_0^\infty \frac{2\zeta(1+\alpha\zeta)}{1+\alpha\zeta+\zeta^2}\, e^{-\zeta^2\sigma}\,d\zeta \ . \tag{23}$$

Using the change of integration variable $y = \zeta^2\sigma$, it follows that

$$\chi(\sigma) = \int_0^\infty G(y,\sigma) e^{-y}\,dy \ , \tag{24}$$

where

$$G(y,\sigma) = \frac{\sigma^{1/2} + \alpha y^{1/2}}{\sigma^{3/2} + \alpha\sigma y^{1/2} + y\sigma^{1/2}} \ . \tag{25}$$

For fixed values of y (real and positive), $G(y,\sigma)$ has the same analytic properties in the complex σ plane as $\chi(\sigma)$. The analytic continuation can be made on both sides of Eq. (24). From Eq. (25), it follows that

$$-\frac{1}{\pi}\lim_{\epsilon\to 0^+} \operatorname{Im}G(y, \sigma = -x + i\epsilon) = \frac{\alpha}{\pi\sqrt{x}}\,\frac{y^{3/2}}{(y-x)^2 + \alpha^2 xy} \ . \tag{26}$$

Equations (22), (24), and (26) therefore imply that

$$\psi(x) = \frac{\alpha}{\pi\sqrt{x}}\int_0^\infty \frac{y^{3/2}e^{-y}}{(y-x)^2+\alpha^2 xy}\,dy \ . \tag{27}$$

Equations (11) and (27) represent the formal solution of the hydrodynamic calculation of the velocity autocorrelation function in Eq. (4).

IV. CONCLUSIONS

Since hydrodynamic claculations of autocorrelation functions are only valid for long (i.e., macroscopic) times,[7] the formal solution should be evaluated as $t\to\infty$. Equation (27) has the asymptotic expansion

$$\psi(x) = (3\alpha/4\sqrt{\pi})x^{-5/2} + O(x^{-7/2}), \quad x\to\infty \ ; \tag{28}$$

therefore

$$(M/kT)\phi(t) = (\alpha/2\sqrt{\pi})(\gamma t)^{-3/2} + \cdots \quad \text{as } t\to\infty \ . \tag{29}$$

The power-law decay $\phi(t) \sim t^{-3/2}$ is much slower than the usually assumed exponential decay $\phi(t)\sim e^{-\gamma t}$, which we have shown to be inconsistent with hydrodynamics. Qualitatively, the hydrodynamic prediction for $\phi(t)$ decreases monotonically from kT/M to zero in the interval $0 < t < \infty$.

Will the power-law decay $\phi(t)\sim t^{-3/2}$ occur in real liquids? This decay will dominate the exponential decay in all fluids where the parameter α is appreciable, i.e., in all fluids where the mass density of the impurity is comparable to the mass density of the fluid. In gases the exponential decay represents a fairly valid description. In dense liquids where ρ is comparable to $3M/4\pi R^3$ exponential decay will not be valid.

Can the power-law decay $\phi(t)\sim t^{-3/2}$ be observed? Although diffusion coefficients (and hence mobilities) have often been measured in the laboratory, this is not true of $\phi(t)$. However, $\phi(t)$ for a fluid made up of hard-sphere molecules has recently been calculated on a computer by Alder and Wainwright.[8] They see clear evidence of a $t^{-3/2}$ law and attribute this behavior to macroscopic fluid mechanics. Their hydrodynamic calculation[8] "... differs conceptually from the Stokes-Einstein model ... ." We have shown that no conceptual differences need be invoked. The relation $D = kT/6\pi\eta R$ is not inconsistent with $\phi(t)\sim t^{-3/2}$. In fact, both follow from the same model.

*Supported by National Science Foundation Grant No. GP-9041.

[1]A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956).
[2]M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. 17, 327 (1945).
[3]E. Nelson, *Dynamical Theories of Brownian Motion* (Princeton U. P., Princeton, N. J., 1967).
[4]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959), pp. 96–99.
[5]R. Kubo, Rept. Progr. Phys. 29 235 (1966).
[6]F. G. Tricomi, *Integral Equations* (Interscience, New York, 1965).
[7]L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963).
[8]B. J. Alder and T. E. Wainwright, Phys. Rev. A 1, 18 (1970).

PHYSICAL REVIEW A VOLUME 3, NUMBER 4 APRIL 1971

Numerical Solutions to the Continuity Equation in the Negative-Glow–Faraday-Dark-Space Transition*

W. B. Hurt
University of Texas, Dallas, Texas 75230
(Received 30 July 1970)

The one-dimensional charged-particle continuity equation with recombination-volume loss terms has been solved in a negative-glow–Faraday-dark-space environment without the usual assumptions neglecting the dependence of electron transport and recombination coefficients on the electric field. It is concluded that such assumptions are in serious error in the one-dimensional case and this raises the question of their effect on a three-dimensional model.

I. INTRODUCTION

The Faraday dark space and negative glow are familiar phenomena in glow discharges, and there is general agreement as to the important atomic processes that should be included in any theoretical discussion of these regions.[1,2] The negative glow is characterized as a low-field high-charge-density plasma with a beam of high-energy electrons from the cathode-fall region being injected into its cathode edge. The effect of this beam is increasingly restricted to the cathode-fall–negative-glow boundary at pressures greater than 1 Torr. Also, at such higher pressures and for sufficiently large discharge dimensions, diffusion loss becomes subordinate to electron-ion recombination loss.[3–5] This is the type of discharge environment with which this present discussion is concerned. On proceeding farther from the cathode-fall region presumably one comes to a point that, due to the loss in charged particles, the electric field has risen to such a value that the recombination rate is reduced considerably and has become subordinate to the diffusion loss rate. This is generally thought to be the condition which distinguishes the Faraday dark space from the negative glow. Consequently, for the discharge environment outlined above the continuity equation in the negative glow sufficiently far from the cathode-fall boundary becomes

$$\nabla^2 N = (\alpha/D_a) N^2 \,, \tag{1}$$

where α is the recombination coefficient and D_a is the ambipolar diffusion coefficient. In the Faraday dark space, the continuity equation becomes

$$\nabla^2 N = 0 \,. \tag{2}$$

In general, these regions are considered separately with an assumed sharp boundary between them and with the mobility, diffusion, and recombination parameters assumed to have constant but different values in the two regions. It is also generally recognized that this boundary is an artificial concept, that its location is arbitrary, and that there is actually a continuous transition from the negative glow to the Faraday dark space.

Also neither of the preceding equations includes any explicit dependence on the current density, one of the most important parameters from an experimental standpoint. The obvious response to this observation with regard to Eq. (1) is that α and D_a are dependent on the electric field, which is in turn dependent on the current density. However, Eq. (2) implies that there is no recombination in the Faraday dark space, and consequently the only possible current dependence of the charge distribution in this region is through the boundary conditions at the negative-glow–Faraday-dark-space interface, an impractical concept as discussed above.